Microstructural and mechanical characterization of annealed tungsten (W) and potassium-doped tungsten foils

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A B S T R A C T

Here we show that potassium-doped tungsten foil should be preferred to pure tungsten foil when considering tungsten laminate pipes for structural divertor applications. Potassium-doped tungsten materials are well known from the bulb industry and show an enhanced creep and recrystallization behaviour that can be explained by the formation of potassium-filled bubbles that are surrounding the elongated grains, leading to an interlocking of the microstructure. In this way, the ultra-fine grained (UFG) microstructure of tungsten foil can be stabilized and with it the extraordinary mechanical properties of the foil in terms of ductility, toughness, brittle-to-ductile transition, and radiation resistance.

In this paper we show the results of three-point bending tests performed at room temperature on annealed pure tungsten and potassium-doped tungsten foils (800, 900, 1000, 1100, 1200, 1300, 1400, 1600, 1800, 2000, 2200, and 2400 °C for 1 h in vacuum). The microstructural assessment covers the measurement of the hardness and analyses of fractured surfaces as well as a comparison of the microstructure by optical microscopy.

The results show that there is a positive effect of potassium-doped tungsten foils compared to pure tungsten foil and demonstrate the potential of the doped foil.

Introduction

Recrystallization and ageing appear to be one of the most critical issues when using W laminate pipes for structural divertor applications [1–3]. While ageing deals with the aspects of the evolution of the W-interlayer interface and therewith the diffusion of W into the interlayer and vice versa [4], recrystallization deals with the microstructural change of the tungsten foil itself.

As the extraordinary mechanical properties of the foil in terms of ductility [5,6], toughness [7,8], brittle-to-ductile transition (BDT) [9], and radiation resistance [10] can be related to the positive influence of cold rolling and the ultra-fine grained (UFG) microstructure, stabilization of the microstructure is essential. However for technically pure tungsten (99.97 wt.% W), the higher the degree of cold work, the lower the recrystallization onset temperature.

So with regard to the use of a W laminate pipe as a structural component for a helium-cooled divert combined with the requirement for an operation condition of two full power years, two main scientific questions have to be addressed:

(1) How can the UFG microstructure be stabilized?
(2) How can the recrystallization temperature be shifted to higher temperatures?

Here, oxide-dispersion strengthened (ODS) tungsten materials [11–13] or potassium (K)-doped tungsten materials [14,15] may offer a solution. The latter is what we assess within this study.

The discovery of potassium-doped W goes back to the early days of wire fabrication (1910–1925) [16,17]. In those days, pure tungsten wires used as filaments in incandescent lamps tended to fail under their own weight. In order to increase the lifetime, so-called non-sag tungsten (NS tungsten) or, as it is also called, doped tungsten was invented. Its improved properties in terms of creep resistance and recrystallization are due to a soft-dispersion-strengthening mechanism, because potassium-filled bubbles, which are gaseous at elevated temperature, surround the elongated grains, leading to an interlocking of the microstructure [18,19].

The production of non-sag tungsten starts by adding aqueous solutions of potassium silicate and aluminium chloride or nitride to the tungsten blue oxide (AKS doping). In the subsequent fabrication steps like hydrogen reduction and acid washing, potassium alumina silicates are incorporated in the grains. Finally, during sintering under hydrogen the potassium alumina silicates dissociate and both aluminium (Al) and silicon (Si) are removed by diffusion and volatilization. The potassium (K) remains in the grains as insoluble bubbles in the tungsten matrix

[16]. In order to establish the desired interlocking microstructure, a high degree of work is needed. In a wire, typical potassium bubbles are elongated in rows and have a size of 20–40 nm.

More details about the fabrication process, the thermochemistry of the K bubbles, a discussion about tungsten-wire-reinforced metals, and applications of non-sag tungsten can be found elsewhere [17]. Furthermore the fracture behaviour of K-doped tungsten plate and rod materials has been assessed and discussed with respect to other tungsten materials [20]. Finally, there are publications dealing with the enhanced creep resistance [21–23] and recrystallization behaviour [24–26] of K-doped tungsten wire compared to pure tungsten wire.

Tungsten foil experienced a very high degree of cold work, resulting in a pronounced crystallographic texture in {001} < 110 > (rotated cube), pancake-shaped grains with dimensions of 0.5 μm × 3 μm × 15 μm, a predominantly sub-grained microstructure, and a high rolling-induced dislocation density [9]. Based on this microstructure, the extraordinary recrystallization behaviour of W foil has to be discussed.

In chronological order, a distinction should be made between recovery, recrystallization, and grain growth [27]. The driving force for recovery is the stored energy due to point and line defects. Recovery consists of three levels, which are dislocation annihilation, dislocation rearrangement, and sub-grain growth, and results in nucleation formation. The driving force for recrystallization (also called primary recrystallization) is the stored energy due to dislocations and is defined as the movement of high-angle grain boundaries. The driving force for grain growth (called secondary recrystallization for the development of a bimodal grain size distribution) is the elimination of boundary area. Especially for semi-finished products that experienced a high degree of deformation, secondary recrystallization is likely to take place. Finally, there is ternary recrystallization, which is driven by surface energy and might take place if the grain size exceeds the thickness of the plate [28]. For tungsten foil, due to the high degree of cold work and the big free surface, secondary and ternary recrystallization has to be taken into account.

Our former work shows that for technical pure tungsten foil, there is no nucleation formation but only grain growth. The means that the sharp rotated cube texture in the as-rolled condition becomes even more pronounced during annealing and that a quasi-single crystal can be produced [9].

In general the recrystallization process of technically pure W is characterized by decreasing start temperature with increasing deformation. However, as described above, the situation appears to be different for potassium-doped W. Here, the higher the degree of deformation, the more finely dispersed the K bubbles, the more effective the grain boundary stabilization, and thereby the higher the recrystallization temperature. This description shows that a minimum of plastic deformation is needed to make this mechanism work. So the question that arises is whether or not the positive effect of the K bubbles can already be found in 200 μm W foil.

The following questions will be answered in this paper:

(1) What does the recrystallization behaviour of technically pure and potassium-doped W foil look like?
(2) What is the evolution of the microstructure, hardness, and fracture behaviour?
(3) Can benefit be gained even for 200 μm thin foil, or is a higher degree of deformation needed?

Experimental methods

Materials and microstructure

The materials used for this investigation are rolled 99.97% pure tungsten (W) and potassium (0.005 wt.%) doped tungsten (WVM) foils with thicknesses of 200 and 215 μm, respectively. These are commercially available materials produced by PLANSEE SE, Reutte (Austria) by a powder metallurgical route. After sintering, they were hot and cold rolled with a high degree of deformation, which resulted in elongated grains (Fig. 1). The received foils were cut into samples with dimensions of 10 × 15 mm^2. The samples of both materials underwent heat treatment by annealing at different temperatures: 800, 900, 1000, 1100, 1200, 1300, 1400, 1600, 1800, 2000, 2200, and 2400 °C, for 1 h in vacuum.

For the microstructural study, the samples were embedded in a hard resin to obtain a hard and stiff compound that prevents delamination of the cross-sections during grinding and mechanical polishing [9]. Then, to reveal the microstructure, the materials were etched with the proper solution (10 g KOH, 10 g $K_3Fe(CN)_6$ and 100 ml distilled water) during 1 min.

Mechanical tests

Vickers tests, using an applied load of 0.98 N, were performed to measure the microhardness of the W and WVM foils in the as-received condition as well as after the heat treatment at the different temperatures. For each material and annealing temperature no less than six measurements were executed under each condition. We also performed three-point bending (TPB) tests at room temperature (RT) on the W and WVM samples with dimensions of 10 × 15 × 0.200 and 10 × 15 × 0.215 mm^3, respectively. These tests were performed using displacement control at a rate of 10 mm/min and a load span of 10 mm. Due to the limitation of the material available, only one test was executed per each material at the different temperatures.

Finally, the microstructure and fracture surface of the tested samples were analysed using optical and scanning electron microscopy (SEM) to check the evolution of the recrystallization and the relationship with the macroscopic behaviour.

Results and discussion

In the results of the Vickers microhardness test (Fig. 2) we can distinguish three areas:

- In the as-received condition, both foils (W, WVM) have the same hardness of around 580 HV0.1. This value remains nearly constant

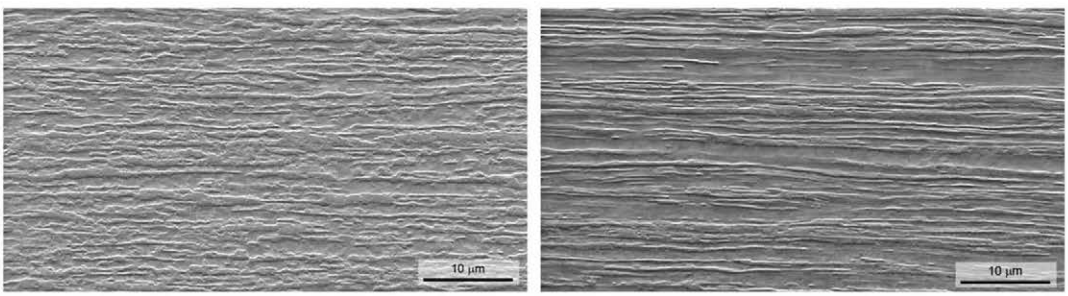

Fig. 1. Scanning electron micrograph cross-sections of the W (left) and WVM (right) foils in the as-received condition. After sintering, materials were hot and cold rolled so elongated grains can be distinguished, the rolling direction can be observed from left to right.

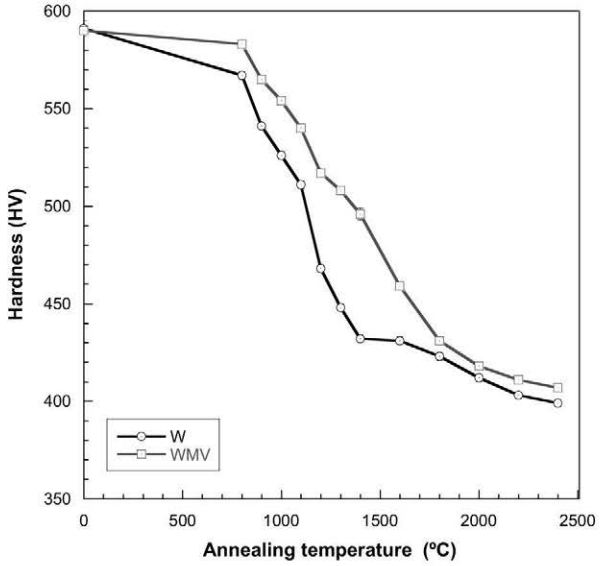

Fig. 2. Vickers hardness (HV0.1) of the W and WVM foils after annealing at different temperatures for 1 h.

for the WVM foil annealed for 1 h at 800 °C, and experiment a small decrease for the W foil under the same condition.

- Increasing the annealing temperature (above 1 h/800 °C), both materials experiment a strong decrease of the hardness up to around 420 HV0.1. The reduction of the hardness is more pronounced in the W than in the WVM foil, it occurs at 1400 °C and 1800 °C, respectively. This slight hardening of the WVM foil is similar to that observed in W foils of 100 μm thickness [9].
- Above 1400 °C for W and 1800 °C for WVM, the Vickers microhardness decreases with an almost asymptotic behaviour.

After the TPB tests at RT, samples show no lineal propagation of the cracks in none of the foils (Fig. 3). TPB tests on W foils show a brittle behaviour for all the temperatures. By contrast, WVM foil is completely ductile in the as-received condition, and after annealing for 1 h/800 °C has brittle behaviour but did not break during the TPB test. Delamination of the WVM foils is observed on the WVM foils after the TPB tests (Figs. 3, 4 right).

As mentioned above, the microstructure of both as-received materials is laminar with fine grains oriented along the rolling direction due to the rolling fabrication process (Fig. 1). Further analysis of the fracture surfaces after the TPB tests at RT reveals that both materials annealed for 1 h at 1000 °C preserve the laminar structure and the fine grains (Fig. 4). The fracture surface of the WVM foil also shows the delamination produced during the TPB test (Fig. 4, right).

However, when we increase this annealing temperature to 1100 °C, the W foil (Fig. 5, left) experiences recrystallization of some grains, even though it still maintains the elongated structure from the deformation process during fabrication. By contrast, WVM foil (Fig. 5, right) has a very pronounced elongated structure along the rolling direction and no signs of recrystallization in the grains.

With heat treatment at 1200 °C for 1 h, the difference between the two materials becomes more obvious (Fig. 6). While W foil shows coarse recrystallized grains, WVM foil still exhibits elongated structure. This difference between the fracture surfaces is consistent with the results of the Vickers microhardness tests (Fig. 2), since at 1200 °C the value for the W foil drops and the difference from the doped W becomes larger. This tendency remains constant in the material annealed for 1 h at 1300 °C, but again at 1400 °C we can observe a big contrast between the two materials. This is evident not only in the results of the microhardness test (Fig. 2) but also in the analysis of the fracture surfaces. W foil (Fig. 7, left) shows coarse recrystallized grains with intergranular fracture between the grain boundaries. Instead, the fracture surface of the WVM foil (Fig. 7, right) shows smaller grains with some elongated structure and the transgranular fracture of the bigger grains.

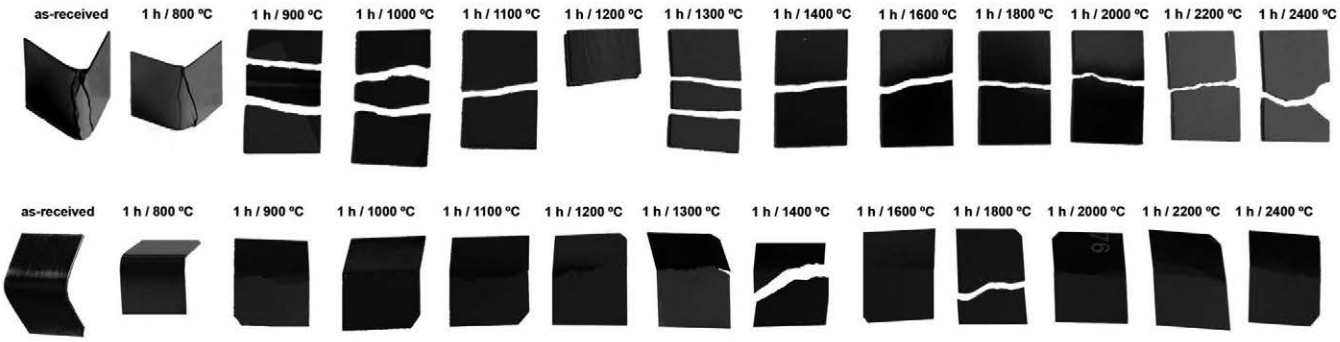

Fig. 3. Foil status after the TPB tests performed in air at RT in the samples with dimensions of 10 × 15 mm2. The upper image shows W foils and the bottom image shows WVM foils.

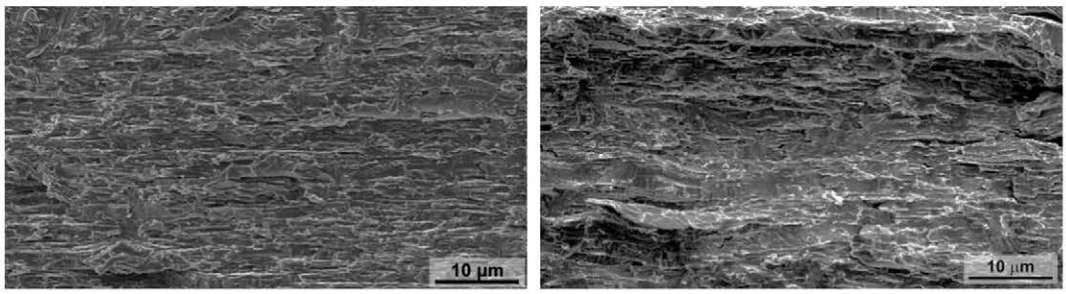

Fig. 4. Fracture surfaces of the W (left) and WVM (right) foils after the TPB tests of samples annealed for 1 h at 1000 °C.

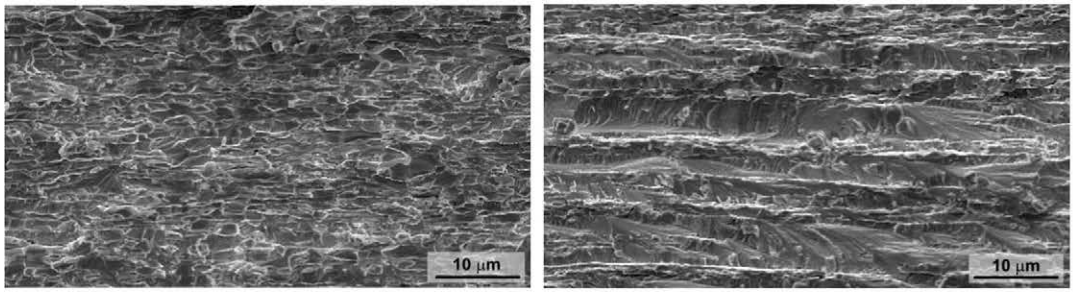

Fig. 5. Fracture surfaces of the W (left) and WVM (right) foils after the TPB tests of samples annealed for 1 h at 1100 °C.

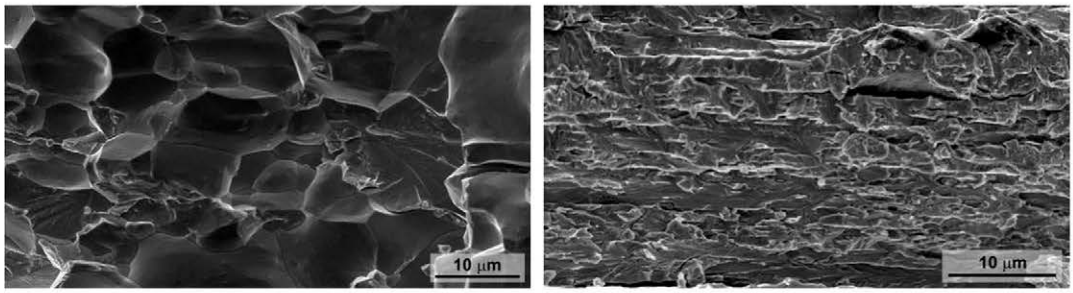

Fig. 6. Fracture surfaces of the W (left) and WVM (right) foils after the TPB tests of samples annealed for 1 h at 1200 °C.

With increasing temperature of the annealing, the contrast in the evolution of the two foils can be observed clearly in the optical micrographs of the cross-sections (Fig. 8). W foil continues to experience grain growth until 2400 °C, at which temperature we can find huge grains as big as the sample thickness. Meanwhile, we observe that the small addition of potassium stabilizes the recrystallization to such an

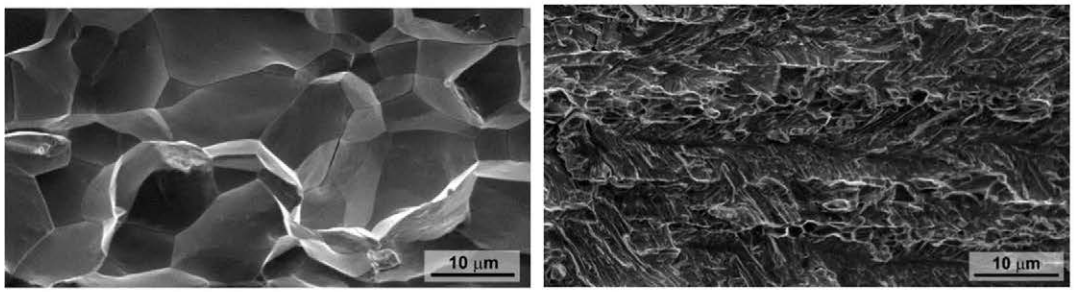

Fig. 7. Fracture surface of the W (left) and WVM (right) foils after the TPB tests of samples annealed for 1 h at 1400 °C.

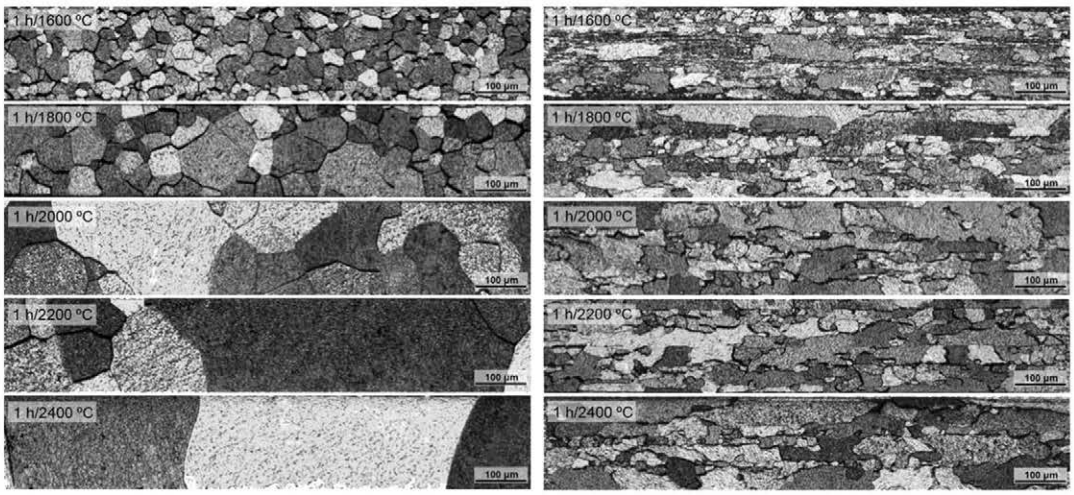

Fig. 8. Optical micrographs of cross-sections with different annealing conditions of the W (left) and WVM foils (right), showing the evolution of the recrystallization at higher temperatures.

extent that foil annealed for 1 h at 2400 °C still shows some elongated structure along the cross-section.

Conclusions

With the addition of 0.005% potassium to the tungsten foils of 0.2 mm thickness, the following conclusions can be drawn:

- Vickers microhardness results indicate a slight enhancement of the values. Although this improvement is visible in foils annealed for 1 h at 800 °C, it becomes more pronounced at 1 h/1400 °C with an increase of 15% in the hardness value. This difference is also observed during the analysis of the fracture surfaces: W foil exhibits coarse recrystallized grains with mostly intergranular decohesion of grain boundaries, while WVM preserves the laminar structure and transgranular fracture in most of the surface.
- The analysis of the samples after the TPB tests shows that W foils are brittle but WVM foils are ductile in the as-received condition and that most of the samples tested did not break during testing but delaminated. This delamination was also observed during the analysis of the fracture surfaces.
- As observed in the optical and scanning electron micrographs, W foil exhibits recrystallization from foils annealed at 1 h/1000 °C. At 1200 °C and until 2400 °C, W foils exhibit increasing grain growth and disappearing of the elongated structure. In contrast, although WVM foil exhibits recrystallization at higher temperatures, it preserves the laminar microstructure even at 2400 °C.

In general, we see that potassium stabilizes the recrystallization of the tungsten grains and helps to preserve the fine and elongated structure even in foils annealed at 2400 °C for 1 h.

In summary, the results show a slightly positive effect of the potassium-doped foil, but it is very likely that much higher degrees of cold work are needed to improve the K bubbles interlocked microstructure. Potassium-doped tungsten foils promise enhanced creep behaviour and show potential for an enhanced recrystallization onset temperature of perhaps 1400–1600 °C. So for technical applications, potassium-doped tungsten foil should be preferred to technically pure tungsten.

Furthermore, ongoing work might look more closely at the extraordinary recrystallization behaviour of tungsten foils in general, as tungsten foils show no nucleation but only grain growth.

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